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(72) Inventors:
• **Abusleme, Julio A.**
21047 Saronno, Varese (IT)
• **Manzoni, Claudia**
40100 Bologna (IT)
• **Besana, Gaimbattista**
22066 Mariano Comense, Como (IT)

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(71) Applicant: **Ausimont S.p.A.**
20121 Milano (IT)

(74) Representative: **Sama, Daniele, Dr. et al**
Sama Patents
Via Morgagni, 2
20129 Milano (IT)

(54) **Multilayers of polyamides and CPVC**

(57) A multilayer comprising at least one layer A) of at least one thermoprocessable polymer containing at least 5% by weight of chlorinated polyvinyl chloride (CPVC) and one layer B) based on polyamides having an amount of -NH₂ end groups in the range 20-300 µeq/g.

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Description

[0001] The present invention relates to multilayers (laminates) comprising at least one polymer layer containing at least 5% of chlorinated polyvinyl chloride (CPVC) and one polyamide layer, characterized in having a complete adhesion among the layers. The adhesion between the layers is so high that at the delamination tests the specimen breaks without the layer separation.

[0002] Said multilayers show, besides a high adhesion among the layers, good mechanical properties, good chemical and flame resistance.

[0003] It is known that polyamides have good mechanical properties but a poor resistance to flame and to chemical agents. CPVC shows a poor ductility but has a good resistance to flame and to chemical agents.

[0004] The need was therefore felt to have available laminates showing the good mechanical properties of the polyamides combined with the good resistance to flame and to chemical agents of CPVC.

[0005] CPVC contains from 58% to 75% by weight of chlorine and is obtained by PVC chlorination.

[0006] The polyvinylchloride (PVC) has a chlorine content of 56.8% by weight.

[0007] Tests carried out by the Applicant have shown that by a bilayer of CPVC polymers with polyamides, obtained for example by applying a pressure on the overlapped polymer layers maintained at the softening temperature or by co-extruding the layers, the adhesion is not obtained.

[0008] The Applicant has surprisingly and unexpectedly found that it is possible to obtain multilayers, having a complete adhesion between CPVC and polyamides when polyamides are characterized by having an amount of $-NH_2$ end groups of at least 20 $\mu eq/g$.

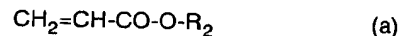
[0009] An object of the present invention is therefore a multilayer comprising at least one bilayer (laminate) between:

A) a layer of at least one thermoprocessable polymer containing at least 5% by weight of chlorinated polyvinyl chloride (CPVC) having a chlorine content from 58% to 75% by weight, preferably from 60% to 70% by weight;

B) a layer based on polyamides having an amount of $-NH_2$ end groups in the range 20-300 $\mu eq/g$, preferably 30-150 $\mu eq/g$.

[0010] The thermoprocessable polymer of layer A) can be selected from PVC and/or polyvinylidene chloride (PVDC). Preferably layer A) is formed by CPVC.

[0011] Optionally layer B) of the bilayer A/B can be placed on top of another layer A) or on top of layer C) based on thermoprocessable copolymers of ethylene with chlorotrifluoroethylene (CTFE), and/or tetrafluoroethylene (TFE), preferably CTFE, and with acrylic monomers of formula:



wherein R_2 is H or a linear or branched C_1-C_{20} alkyl radical, cycloalkyl radical; R_2 optionally contains Cl, O, N and/or one or more functional groups selected from -OH, -COOH, epoxide, ester or ether; wherein the monomer (a) amount is in the range 0.01-15% by moles with respect to the sum of the monomers of ethylene and of CTFE and/or TFE.

[0012] The thermoprocessable copolymers of layer C) are preferably formed by:

- from 10% to 70% by moles, preferably from 35% to 55% of ethylene;
- from 30% to 90% by moles, preferably from 45% to 65%, of a fluorinated monomer selected from tetrafluoroethylene, chlorotrifluoroethylene, or mixtures thereof;
- from 0.05% to 15% by moles of the acrylic co-monomer (a) referred to the sum of the previous monomers.

[0013] As acrylic monomer of formula (a), n-butylacrylate (n-BuA) is preferably used.

[0014] The layer C) can also be formed by a blend of the copolymers of layer C) and the thermoprocessable copolymers of ethylene with chlorotrifluoroethylene (CTFE) and/or tetrafluoroethylene (TFE), provided that the blend contains an amount of acrylic monomer (a) in the range 0.01%-15% by moles with respect to the total sum of the monomers of ethylene and of CTFE and/or TFE of the blend.

[0015] Preferably in layer C) the monomer amount of (a) is lower than 1% by moles with respect to the sum of the monomers of ethylene and chlorotrifluoroethylene and/or tetrafluoroethylene.

[0016] Optionally on top of layer C) of the multilayer A/B/C, can be put a layer C1) formed by thermoprocessable copolymers of ethylene with chlorotrifluoroethylene (CTFE) and/or tetrafluoroethylene (TFE).

[0017] On top of layer A) of the bilayer A/B another layer B) can be put, which can be further in contact with a layer C) and subsequently on layer C) can be placed a layer C1). Examples of possible multilayers are:

- A/B/A
- A/B/C
- A/B/C/C1
- B/A/B
- C/B/A/B
- C1/C/B/A/B
- C/B/A/B/C
- C1/C/B/A/B/C
- C1/C/B/A/B/C/C1

[0018] In a multilayer that ends with layer B, optional-

ly, on this layer can be placed a layer B1) formed by a polyamide with a content of -NH_2 end groups lower than $20 \mu\text{eq/g}$.

[0019] The polyamides having an amount of -NH_2 end groups, higher than $20 \mu\text{eq/g}$, can be prepared according to known methods, for example according to USP 4,543,378, wherein a chain transfer agent is used in the polymerization phase. As example of chain transfer agents, m- or p-xylylen-diamine, hexamethyldiamine or dodecamethyldiamine can be cited.

[0020] The polyamide of layer B) having an amount of end groups -NH_2 higher than $20 \mu\text{eq/g}$ can also be obtained by mixing polyamides having different contents of -NH_2 end groups so that the final mixture contains an amount of -NH_2 end groups higher than $20 \mu\text{eq/g}$.

[0021] The polyamides of layer B), can be a (co)polyamide, for example, polyamide 6 (PA 6), polyamide 66 (PA 66), polyamide 11 (PA 11), polyamide 12 (PA 12).

[0022] The polyamides of layer B), can optionally contain diamines.

[0023] The Applicant has also found that the multilayers of the present invention endowed with excellent adhesions can be obtained by using as layer B) a blend of a polyamide having an amount of -NH_2 end groups lower than $20 \mu\text{eq/g}$ and 0.1-5% by weight, preferably 0.5-2% by weight, of one or more diamines.

[0024] The polyamides having -NH_2 end groups lower than $20 \mu\text{eq/g}$, can be (co)polyamides, such as for example, polyamide 6, polyamide 66, polyamide 11, polyamide 12.

[0025] Non limitative examples of diamines are protected amines, such as for example hexamethyldiaminecarbamate and N,N'-dicinnamylidene-1,6 hexanediamine, $\text{C}_4\text{-C}_{20}$ aliphatic diamines, such as for example dodecyl diamine and decyl diamine, aromatic diamines, such as for example para-xylyldiamine. Aliphatic and aromatic protected diamines are preferred.

[0026] The single layers of the invention can optionally contain additives such as fillers for example polytetrafluoroethylene (PTFE), silicates, graphite, titanium dioxide, lubricants, pigments, fire retardants, plasticizers, thermal and UV stabilizers.

[0027] The multilayer structures of the present invention can be obtained by co-extrusion. Alternatively, the single layers are laminated by compression at the softening temperature.

[0028] When layer A) and layer C) are formed by self-supporting plaques suitable to build, by their combination, hybrid structures such as for example those used in wet-benches, their junction-coupling can be carried out by welding along a contact line using a weld rod, constituted by the above defined polyamide of layer B).

[0029] Optionally on top of layers A) and C) a layer B) can be placed.

[0030] The multilayers according to the present invention can be used as structural elements for benches,

coating panels, in the building of structures such as, for example, the wet-benches used in the semiconductor industry.

[0031] Some illustrative examples follow, which are not limitative of the present invention.

[0032] The following characterizations were carried out on the polymers of the examples:

- Melt Flow Index (M.I.)

The M.I. of the fluorinated polymers is measured according to the method ASTM 3275-89, at 275°C and with a load of 2.16 kg;

- Second melting temperature (T_{mII})

The T_{mII} of the fluorinated polymers is determined by differential scanning calorimetry (DSC);

- Glass transition temperature (T_g)

The T_g of the polymers CPVC is determined by differential scanning calorimetry (DSC);

- Chlorine content in CPVC

it has been determined by elemental analysis;

- -NH_2 End groups

The number of the end groups -NH_2 of polyamides is determined by preparing a solution at 2% of polyamide in m-cresol and subsequent titration with perchloric acid.

EXAMPLES

EXAMPLE 1

Layer A)

CPVC

[0033] From a CPVC polymer having a T_g of 112°C and a chlorine content of 64.24% by weight, plaques having a thickness of 1.5 mm have been obtained by compression moulding.

Layer B)

Polyamide 12 (PA 12) having -NH_2 end groups equal to $110 \mu\text{eq/g}$

[0034] Some plaques of the polyamide having a thickness of 1.5 mm have been obtained by compression moulding.

Preparation of the A/B laminate

[0035] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0036] By applying a mechanical force one tries to separate layer A from layer B.

[0037] One cannot measure the adhesion force between layer A and layer B. By increasing the force to separate the layers, one breaks the manufactured arti-

cle without obtaining the delamination. This shows that the laminate according to the invention shows a high adhesion.

EXAMPLE 2 (comparative)

Layer A)

[0038] The same polymer of Example 1 is used.

Layer B)

PA 12 having -NH₂ end groups equal to 13 µeq/g

[0039] Some plaques of the polyamide having a thickness of 1.5 mm have been obtained by compression moulding.

Preparation of the A/B laminate

[0040] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0041] The A/B laminate does not show any adhesion between the layers.

EXAMPLE 3 (comparative)

Layer A)

[0042] The same polymer of Example 1 is used.

Layer B)

PA 12 having -NH₂ end groups equal to 18 µeq/g

[0043] The polyamide has been obtained by mechanically mixing 50 g of PA 12 of Example 1 (-NH₂ = 110 µeq/g) with 950 g of PA 12 of Example 2 (-NH₂ = 13 µeq/g). Then the blend has been pelletized in a single screw Brabender extruder in Hastelloy C-276 having a diameter of 18 mm and a length equivalent to 25 times the diameter, with a melt temperature of 225°C. Plaques having a thickness of 1.5 mm have been prepared from the granules by compression moulding.

Preparation of the A/B laminate

[0044] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0045] The A/B laminate does not show any adhesion between the layers.

EXAMPLE 4

Layer A)

5 [0046] The same polymer of Example 1 is used.

Layer B)

PA 12 having -NH₂ end groups equal to 23 µeq/g

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[0047] The polyamide has been obtained by mechanically mixing 100 g of PA 12 of Example 1 (-NH₂ = 110 µeq/g) with 900 g of PA 12 of Example 2 (-NH₂ = 13 µeq/g). Then the blend has been pelletized in a single screw Brabender extruder in Hastelloy C-276 having a diameter of 18 mm and a length equivalent to 25 times the diameter, with a melt temperature of 225°C. Plaques having a thickness of 1.5 mm have been prepared from the granules by compression moulding.

15

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Preparation of the A/B laminate

[0048] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

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[0049] By applying a mechanical force one tries to separate layer A from layer B.

30

[0050] One cannot measure the adhesion force between layer A and layer B. By increasing the force to separate the layers, one breaks the manufactured article without obtaining the delamination. This shows that the laminate according to the invention shows a high adhesion.

35 EXAMPLE 5

Layer A)

[0051] The same polymer of Example 1 is used.

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Layer B)

PA 12 having -NH₂ end groups equal to 32 µeq/g

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[0052] The polyamide has been obtained by mechanically mixing 200 g of PA 12 of Example 1 (-NH₂ = 110 µeq/g) with 800 g of PA 12 of Example 2 (-NH₂ = 13 µeq/g). Then the blend has been pelletized in a single screw Brabender extruder in Hastelloy C-276 having a diameter of 18 mm and a length equivalent to 25 times the diameter, with a melt temperature of 225°C. Plaques having a thickness of 1.5 mm have been prepared from the granules by compression moulding.

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55 Preparation of the A/B laminate

[0053] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under

pressure at a temperature of 240°C for 5 minutes.

[0054] By applying a mechanical force one tries to separate layer A from layer B.

[0055] One cannot measure the adhesion force between layer A and layer B. By increasing the force to separate the layers, one breaks the manufactured article without obtaining the delamination. This shows that the laminate according to the invention shows a high adhesion.

EXAMPLE 6

Layer A)

[0056] The same polymer of Example 1 is used.

Layer B)

PA 12 having -NH₂ end groups equal to 45 µeq/g

[0057] The polyamide has been obtained by mechanically mixing 330 g of PA 12 of Example 1 (-NH₂ = 110 µeq/g) with 670 g of PA 12 of Example 2 (-NH₂ = 13 µeq/g). Then the blend has been pelletized in a single screw Brabender extruder in Hastelloy C-276 having a diameter of 18 mm and a length equivalent to 25 times the diameter, with a melt temperature of 225°C. Plaques having a thickness of 1.5 mm have been prepared from the granules by compression moulding.

Preparation of the A/B laminate

[0058] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0059] By applying a mechanical force one tries to separate layer A from layer B.

[0060] One cannot measure the adhesion force between layer A and layer B. By increasing the force to separate the layers, one breaks the manufactured article without obtaining the delamination. This shows that the laminate according to the invention shows a high adhesion.

EXAMPLE 7

Layer A)

[0061] The same polymer of Example 1 is used.

Layer B)

Polyamide PA 12 having -NH₂ end groups equal to 13 µeq/g blended with 1% by weight of diamine

[0062] One kilogram of polyamide (PA 12) in granules, having -NH₂ end groups equal to 13 µeq/g, has been blended with 1% by weight of hexamethylenedi-

amine monocarbamate. Then it has been pelletized in a single screw Brabender extruder in Hastelloy C-276 having a diameter of 18 mm and a length equivalent to 25 times the diameter, with a melt temperature of 225°C. Plaques having a thickness of 1.5 mm have been prepared from the granules by compression moulding.

Preparation of the A/B laminate

10 [0063] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0064] By applying a mechanical force one tries to separate layer A from layer B.

15 [0065] One cannot measure the adhesion force between layer A and layer B. By increasing the force to separate the layers, one breaks the manufactured article without obtaining the delamination. This shows that the laminate according to the invention shows a high adhesion.

EXAMPLE 8

Layer A)

25 [0066] The polymer of Example 1 is used.

Layer B)

30 [0067] The polyamide of Example 1 is used.

Layer C)

E/CTFE/n-BuA 40/55/5% by moles

35 [0068] The copolymer has been prepared by known methods described for example in EP 866 079 and is characterized by:

- 40 - M.I. 15 g/10'
- T_{mll} 180°-200°C.

[0069] Plaques having a thickness of 1.5 mm have been obtained from the copolymer by compression moulding.

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Preparation of the A/B/C multilayer

50 [0070] The plaques of the single layers A, B and C, previously obtained, have been overlapped in the order A/B/C, and kept under pressure at a temperature of 240°C for 5 minutes.

[0071] By applying a mechanical force one tries to separate layer A from layer C of the multilayer A/B/C.

55 [0072] One cannot measure the separation force. This shows that the multilayer of the invention shows a high adhesion among the layers.

EXAMPLE 9Layer A)

[0073] The same polymer of Example 1 is used.

Layer B)

[0074] The same polyamide of Example 6 is used.

Layer C)

[0075] The same copolymer of Example 8 is used.

Preparation of the A/B/C multilayer

[0076] The plaques of the single layers A, B and C, previously obtained, have been overlapped in the order A/B/C, and kept under pressure at a temperature of 240°C for 5 minutes.

[0077] By applying a mechanical force one tries to separate layer A from layer C of the A/B/C multilayer.

[0078] One cannot measure the separation force. This shows that the multilayer of the invention shows a high adhesion among the layers.

EXAMPLE 10Layer A)

[0079] The same polymer of Example 1 is used.

Layer B)

[0080] The same polyamide of Example 7 is used.

Layer C)

[0081] The same copolymer of Example 8 is used.

Preparation of the A/B/C multilayer

[0082] The plaques of the single layers A, B and C, previously obtained, have been overlapped in the order A/B/C, and kept under pressure at a temperature of 240°C for 5 minutes.

[0083] By applying a mechanical force one tries to separate layer A from layer C of the A/B/C multilayer.

[0084] One cannot measure the separation force. This shows that the multilayer of the invention shows a high adhesion among the layers.

EXAMPLE 11 (comparative)Layer A)

[0085] The same polymer of Example 1 is used.

Layer C)

[0086] The same copolymer of Example 8 is used.

Preparation of the A/C laminate

[0087] The plaques of the single layers A and C, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0088] The laminate A/C does not show any adhesion between the layers.

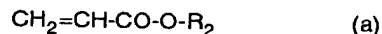
Claims

1. A multilayer comprising at least one bilayer (laminate) between:

A) a layer of at least one thermoprocessable polymer containing at least 5% by weight of chlorinated polyvinyl chloride (CPVC) having a chlorine content from 58% to 75% by weight, preferably from 60% to 70% by weight;

B) a layer based on polyamides having an amount of -NH₂ end groups in the range 20-300 µeq/g, preferably 30-150 µeq/g.

2. A multilayer (laminate) according to claim 1, wherein layer B) of the A/B bilayer is placed on top of layer A) or of layer C) based on thermoprocessable copolymers of ethylene with chlorotrifluoroethylene (CTFE) and/or tetrafluoroethylene (TFE), preferably CTFE, and with acrylic monomers of formula:



wherein:

R₂ is H or a linear or branched, C₁-C₂₀ alkyl radical, cycloalkyl radical; R₂ optionally contains Cl, O, N and/or one or more functional groups selected from -OH, -COOH, epoxide, ester or ether; wherein the monomer (a) amount is in the range 0.01-15% by moles with respect to the sum of the monomers of ethylene and of CTFE and/or TFE.

3. A multilayer according to claims 1-2, wherein the thermoprocessable copolymer of layer A) is formed by polyvinyl chloride (PVC) and/or polyvinylidene chloride (PVDC).

4. A multilayer according to claims 2-3, wherein the thermoprocessable copolymers of layer C) are formed by:

- from 10% to 70% by moles, preferably from 35% to 55% of ethylene;
- from 30% to 90% by moles, preferably from 45% to 65%, of a fluorinated monomer selected from tetrafluoroethylene, chlorotrifluoroethylene, or mixtures thereof;
- from 0.05% to 15% by moles of the acrylic comonomer

(a) referred to the sum of the previous monomers. 10

5. A multilayer according to claims 2, 3, 4, wherein n-butylacrylate (n-BuA) is used as acrylic monomer of formula (a). 15

6. A multilayer according to claims 2-5, wherein layer C) is formed by a blend of the copolymers of layer C) and the thermoprocessable copolymers of ethylene with chlorotrifluoroethylene (CTFE) and/or tetrafluoroethylene (TFE), provided that the blend contains an amount of acrylic monomer (a) in the range 0.01%-15% by moles with respect to the total sum of the monomers of ethylene and of CTFE and/or TFE of the blend. 20 25

7. A multilayer according to claims 2-6, wherein on top of layer C) of the multilayer A/B/C there is a layer C1) formed by thermoprocessable copolymers of ethylene with chlorotrifluoroethylene (CTFE) and/or tetrafluoroethylene (TFE). 30

8. A multilayer according to claims 1-7, wherein on top of layer A) of the bilayer A/B there is a layer B); on the latter layer there is optionally in sequence a layer C) and a layer C1). 35

9. A multilayer according to claims 1-8, wherein when the multilayer ends with layer B), on this layer there is a layer B1) formed by a polyamide with a content of -NH₂ end groups lower than 20 µeq/g. 40

10. A multilayer according to claims 1-9, wherein the polyamide of layer B) having an amount of -NH₂ end groups higher than 20 µeq/g is obtained by mixing polyamides having different contents of -NH₂ end groups so that the final mixture contains an amount of -NH₂ end groups higher than 20 µeq/g. 45

11. A multilayer according to claims 1-10, wherein layer B) is a blend of a polyamide having an amount of -NH₂ end groups lower than 20 µeq/g and 0.1-5% by weight, preferably 0.5-2% by weight, of one or more diamines. 50 55

12. A multilayer according to claim 11, wherein the diamines are selected from the group formed by: hexamethylenediaminecarbamate, N,N'-dicinnamyl-

dene-1,6 hexandiamine, C₄-C₂₀ aliphatic diamines, such as dodecylamine and decylamine, aromatic diamines, such as para-xylylenediamine.

- 5 13. Structures as wet-benches obtained by welding the multilayer according to claims 1-12, wherein a welding layer of polyamide B) interposed and/or in contact with the surfaces A) and C) to be put together, is used.

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(71) Applicant: **Ausimont S.p.A.**
20121 Milano (IT)

(72) Inventors:
• **Abusleme, Julio A.**
21047 Saronno, Varese (IT)
• **Manzoni, Claudia**
40100 Bologna (IT)
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Sama Patents
Via Morgagni, 2
20129 Milano (IT)

(54) **Multilayers of polyamides and CPVC**

(57) A multilayer comprising at least one layer A) of at least one thermoprocessable polymer containing at least 5% by weight of chlorinated polyvinyl chloride (CPVC) and one layer B) based on polyamides having an amount of -NH₂ end groups in the range 20-300 µeq/g.

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EUROPEAN SEARCH REPORT

Application Number
EP 02 01 1820

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 1 101 994 A (TOKAI RUBBER IND LTD) 23 May 2001 (2001-05-23) * claims 1,2,6,7 * * page 2, line 42 - line 44 * * page 3, line 31 - line 47 * * page 4, line 25 - page 5, line 57 * ----	1-13	B32B27/08 B32B27/34 B32B27/30
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A	EP 1 038 914 A (AUSIMONT SPA) 27 September 2000 (2000-09-27) * claims 1,13-16 * * page 2, line 41 - line 53 * * page 3, line 36 - line 45 * ----	1-13	
A	US 4 183 777 A (KLINER GEORGE J ET AL) 15 January 1980 (1980-01-15) * claim 1 * * column 1, line 26 - line 34 * * column 3, line 43 - line 47 * * column 6, line 41 - line 48 * * example 4; table 8 * -----	1-13	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
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Place of search THE HAGUE		Date of completion of the search 22 November 2002	Examiner Girard, S
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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